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## H<sub>2</sub>CAP – Hydrogen assisted catalytic biomass pyrolysis for green fuels

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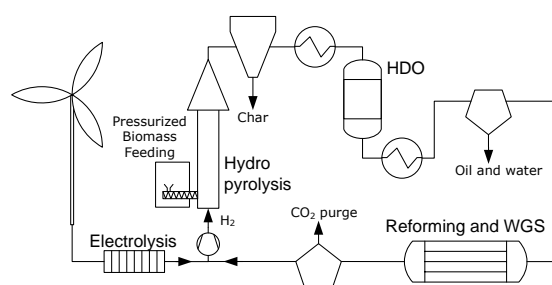
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*Biomass such as wood, straw and energy crops are considered renewable sources of carbonaceous fuels, however biomass is still a limited resource. It is therefore desirable to utilize biomass where no other source of renewable energy is readily available, such as fuels for the transportation sector. The objective of the present work is to convert biomass into gasoline and diesel. Fast pyrolysis of beech wood have been conducted at high hydrogen pressure in a fluid bed reactor with a hydrodeoxygenation (HDO) catalyst as bed medium followed by a fixed bed HDO reactor for complete oxygen removal before oil condensation. Dependent on reactor temperatures the organic liquid yield including C<sub>4+</sub> gases varied between 16.3 and 21.3 wt.% daf (dry, ash free basis). The oxygen content of the oil was always <1 wt.%, corresponding to an energy recovery in the oil between 40 and 52 %. Ongoing work includes optimization of reaction conditions and catalysts to improve the yield of oxygen free bio-oil.*

### 1. Scope

Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies [1]. To utilize this oil as transportation fuel the oxygen content must be reduced from 15-30 wt.% down to <1 wt.%, which increases heating value and stability and decreases acidity<sup>1</sup>. Upgrading bio-oil by catalytic hydrodeoxygenation (HDO) is challenged by severe polymerization and coking upon heating the oil. Alternatively, performing fast pyrolysis in high-pressure hydrogen atmosphere in a fluid bed reactor with a HDO catalyst as bed medium could immediately stabilize reactive pyrolysis vapors<sup>2</sup>. An additional vapor phase HDO reactor ensures removal of oxygen down to <1 wt.%, resulting in separate hydrocarbon oil and aqueous phases being recovered. A schematic diagram for such a process is shown in Figure 1. A simplified bench scale setup has been constructed at DTU Chemical Engineering. With a capacity of 100 to 300 g/h solid biomass, the aim is to provide a proof-of-concept for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.



**Figure 1.** Simplified H<sub>2</sub>CAP process diagram including fluid bed catalytic hydrolypyrolysis (10 to 40 bar and 350 to 500°C), char separation, temperature adjustment, vapor phase HDO reactor (10 to 40 bar and 300 to 400°C), cooling, condensation, and liquid separation. These parts have been constructed at DTU Chemical Engineering. Additionally, steam reforming and water gas shift (WGS) of non-condensable gasses to H<sub>2</sub> and CO<sub>2</sub> and wind-powered electrolysis of water to H<sub>2</sub> is envisioned.

### 2. Results and discussion

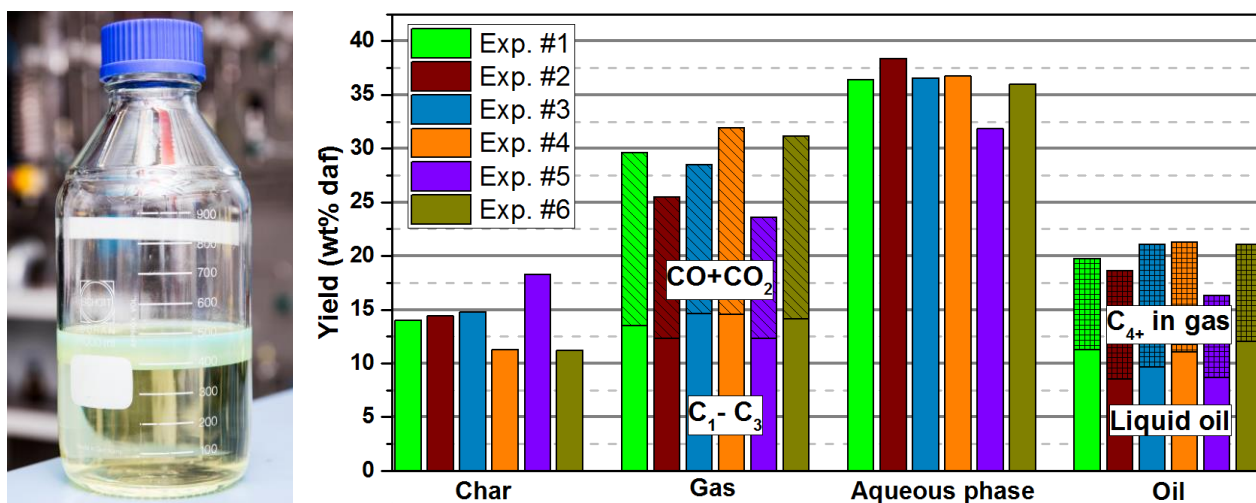
Experiments have been performed using 50 g of a commercial CoMo/MgAl<sub>2</sub>O<sub>4</sub> catalyst in the fluid bed reactor and 173 g of a commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst in the HDO reactor. The catalysts were sulfided at 25 barg with 2-7.5 % of H<sub>2</sub>S, 5 % N<sub>2</sub> in balance H<sub>2</sub> by feeding liquid DMDS to the system. The hydrolypyrolysis of biomass has been performed at 25 barg with gas composition 465-470 ppm H<sub>2</sub>S, 6 % N<sub>2</sub> and balance H<sub>2</sub> at a total flow of 85-87 NL/min. The actual total flow at reaction temperature and pressure corresponds to approximately three times the minimum fluidization velocity ( $3 \cdot u_{mf}$ ) for the employed catalyst sieve fraction. The biomass used was beech wood, bark free and approximate particle size 200 to 700 µm. Moisture 5.75 wt.% (bone dry at 102 °C) and ash content 0.58 wt.% (dry basis).

Table 1 summarizes the reaction conditions in the experiments performed so far. For each experiment a fresh load of catalyst in the fluid bed reactor and the same load of catalyst in the HDO reactor were used, but both catalysts were sulfided before each experiment.

**Table 1:** Reaction conditions employed in the first experiments

	Exp. #1	Exp. #2	Exp. #3	Exp. #4	Exp. #5	Exp. #6
<b>Biomass feed [g/h]</b>	282	194	212	233	239	250
<b>Feed time [h]</b>	3.50	2.60	4.02	4.02	1.22	3.98
<b>Fluid bed Temp. [°C]</b>	425	400	400	470	365	451
<b>HDO Temp. [°C]</b>	375	350	400	390	395	371

A photograph of the condensed liquids from Exp. #4 and the yields obtained from Exp. #1 to #6 are shown in Figure 2. These very first results show that the process performs excellently as intended. The products are phase separated aqueous and hydrocarbon fractions. The low viscosity, free-flowing oil is very different to conventional wood pyrolysis oil. Detailed oil analysis has shown that all the produced oils contain less than 1 wt.% O and that the main oxygenates left in the oil is dibenzofurans and naphthol. The condensed oil consists of 20-40 vol.% naphtha and 60-80 vol.% diesel and contains more than 50 wt.% aromatics. The oil composition is determined by GCxGC-FID. Typical chromatographic area of paraffins is 3.4-4.3 %, naphthenes 35.9-42.5 %, monoaromatics 42.3-46.5 %, diaromatics 8.7-10.3 %, triaromatics 1.7-1.9 %, tetraaromatics 1-1.2 %, and larger aromatics 0-0.1%. The best oil yield is 21.3 wt.% daf of the wood, corresponding to approximately 38 % carbon atom yield and an energy yield of approximately 52 %. The char and gas yield show room for improvement of catalysts and reaction conditions, work which is presently underway.



**Figure 2.** Photograph of recovered liquid from Exp. #4, oil is top phase. Yields of char, C<sub>1</sub>-C<sub>3</sub> hydrocarbons, CO+CO<sub>2</sub>, condensed aqueous phase and condensed oil with potentially condensed oil (C<sub>4</sub>+) in gas phase on dry, ash free basis for Exp. #1 to #6. The mass balances sum to 100 %, 97 %, 101 %, 101 %, 90 %, and 100 % respectively.

### 3. Conclusions

This study confirms that catalytic hydropyrolysis with hydrodeoxygenation is an attractive route for biomass to liquid fuels. The reaction conditions employed is significantly milder than gasification, potentially resulting in lower capital and operating costs, and the energy yield is significantly better than second-generation bio-ethanol. The oil yields are comparable to those reported in literature<sup>2,3</sup>.

### References

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